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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention and LSI It is related with low dielectric constant ingredients, such as an insulator layer used between the layers of a component etc. [0002]

[Description of the Prior Art] LSI Improvement in the speed of a component, It takes to high integration, The problem of signal delay is becoming serious. Signal delay is the resistance R of wiring. Capacity C during wiring and between layers In order to be connected with a product and to suppress delay to min It ranks with reducing wiring resistance, It is an effective means to lower the specific inductive capacity of an interlayer insulation film., Wiring spacing will be integrated highly by about 0.18 micrometers in 2001, and it is specific inductive capacity 2.5. It is said that the ingredient of the following is needed.

[0003] Former, It is a spin-on glass (SOG) about the sol which hydrolyzed and produced tetra-alkoxysilane as an interlayer insulation film. The approach of forming membranes by law is learned. However, the molecular structure of the ingredient which carried out in this way and was produced does not have an opening at all by the three-dimensional network of ****Si-O-Si ****, Specific inductive capacity is 4.0. It was high. as the approach for lowering specific inductive capacity -- CVD etc. -- membrane formation of SiOF to depend, Membrane formation of an organic material, Porous membrane etc. is proposed. SiOF is F. Specific inductive capacity is 3.3 in increase of a content. It is F although it falls to extent. There is a problem that hygroscopicity becomes high with an amount. Organic material, Specific inductive capacity 2.2 Although the low dielectric constant ingredient to extent is obtained The technical problem that thermal resistance and adhesion with a substrate are difficult occurs., Organic [SOG] It is 2.7 although forming a low consistency and lowering specific inductive capacity by introducing an organic radical into SiO₂ is examined by the system. Extent is called limitation. On the other hand, since the specific inductive capacity is changed with the amount of a hole, a porous material is specific inductive capacity 2.5. It is expected as an ingredient of the following.

[0004] as the example of a porous material -- inorganic [SOG] making heat treatment decompose a sililation reagent after forming a sililation reagent and the thing made to react, and introducing about 80nm hole -- specific inductive capacity -- 2.3 up to -- [N.Aoi and Jpn.J.Appl.Phys.36 (1997) 1355] to which the lowered example is reported. However, this film is 13% by moisture absorption in atmospheric air. In there being an increment in the dielectric constant of extent, it is large and the hole introduced is 0.18 micrometers. It is an average of 2 in wiring spacing. Since there is only a hole of an individual, film reinforcement poses a problem.

[0005] Age under ambient atmosphere control after forming the liquid which uses a tetra-ethoxy silane as a start raw material as another example of porous membrane, perform the small solvent and solvent permutation of surface tension, it is made to dry so that the film may not contract at the time of evaporation of a solvent, and there is xerogel film of a detailed hole obtained by processing a front face with a sililation reagent [Mat.Res.Soc.Symp.Proc.443 and 99 (1997)]. However, the top where a production process is complicated, for every process, this xerogel film needs strict management and is considered that a problem is in points, such as repeatability, by actual device production. The basic

frame of this film consists of SiO₄ tetrahedrons. Although the interior of a frame consists of only SiO₄ tetrahedrons, that by which a part of oxygen of SiO₄ tetrahedron was permuted by the organic radical will also exist only in the perimeter and front face of a hole for the organic radical introduced with a sililation reagent.

[0006] It is the specific inductive capacity 2.5 which reformed the hydrogenation silica particle which has Si-H association by hydrogen silsesquioxane (HSQ) on the front face, and formed membranes on it. It is reported as an ingredient of the following [collection No[of the 58th Japan Society of Applied Physics academic lecture meeting lecture / besides Muraguchi / drafts].2 4 p-K -7]. However, not much highly, degasifying of hydrogen begins from 400 **, and the thermal resistance of Si-H becomes remarkable above 450 **. Membranous hygroscopicity will become high if hydrogen ****s. LSI In a process, the annealing temperature of metal wiring is called 450 **, and it can be said that this film is in the compatibility to a process about a problem.

[0007]

[Problem(s) to be Solved by the Invention] This invention, Semiconductor device, Application on electrical circuit components etc. is possible, The silica system porous membrane of low hygroscopic and a low dielectric constant is offered. [0008]

[Means for Solving the Problem] The three-dimensional network in which said technical problem contains (1) siloxane frame contains the tetrahedron which permuted at least one or more of the bridging oxygen of SiO₄ tetrahedron by the organic radical inside a front face and a frame. And the pitch diameter of 10nm or less (hereafter 5nm preferably) directly surrounded in the perimeter by the frame containing the tetrahedron Two morenm It is especially 1nm hereafter. Following Silica system porous membrane characterized by having a detailed opening, (2) Si and O in a three-dimensional network 1 as which the mineral constituent of an except is chosen from B, aluminum, germanium, Ti, Y, Zr, Nb, and Ta Silica system porous membrane given in (1) characterized by being an element beyond a class, (3) (1) characterized by said organic radical containing a methyl group and/or a phenyl group, or silica system porous membrane given in (2), (4) Si and O in a three-dimensional network The mole ratio to Si of said inorganic configuration element of an except is 0.005. It is 0.15 or less above. And the mole ratio of said methyl group to Si and/or a phenyl group is 0.6. It is 1.5 above. (1) characterized by being the following, (2) Or silica system porous membrane given in (3) and (5) BET The specific surface area by law is 100m²/g. Above The contact angle of water And the low hygroscopicity silica system porous membrane of (1), (2), or (3) publications of 90 degrees or more, The semiconductor device which contains silica system porous membrane (6), (1), (2), (3), (4), or given in (5) as an interlayer insulation film, (7) Those with two or more kinds and its pyrolysis temperature a **** and the silica system coat whose inorganic principal component is SiO₂ beyond two kind (T1, T2:T1>T2) at the middle temperature of T1 and T2 [the organic radical combined with Si] Without heat-treating in an inert gas ambient atmosphere, and pyrolysis temperature making the organic radical of T1 decompose, when pyrolysis temperature makes the organic radical of T2 decompose The manufacture approach of the silica system porous membrane characterized by making an opening with a pitch diameter of 10nm or less form into the three-dimensional network containing a siloxane frame, (8) The organic radical which pyrolyzes and forms an opening is a with a carbon numbers of two or more (generally carbon numbers 2-12) alkyl group or its fluoro substitution product. And the manufacture approach of the silica system porous membrane given in (7) characterized by the organic radical which remains into the film, without pyrolyzing being a methyl group or a phenyl group, (9) (A1) -- general formula R1Si (OR)₃ or R1SiX₃ (here -- R1 -- a methyl group or a phenyl group --) R Carbon number 1-4 An alkyl group or a phenyl group, and X F The compound expressed with the halogen of an except, And (B1) general formula R2R3Si (OR)₂ or R2R3SiX₂ (at least one of R2 and R3 sorts is a carbon number 2 here it is the above (generally carbon number 2-12) alkyl group or its fluoro substitution product) They are a methyl group or a phenyl group, and R except it. Carbon number 1-4 An alkyl group or a phenyl group, X F The compound expressed with the halogen of an except is melted to an organic solvent. hydrolyzing -- having obtained -- a solution -- containing -- a silica -- a system -- porous membrane -- formation -- ** - - coating liquid -- (-- ten --) (A2) -- a general formula -- R -- four -- Si -- (-- OR --) -- three -- or -- R --

four -- SiX -- three (here -- R4 -- a carbon number 2 -- the above (generally carbon number 2-12) alkyl group or its fluoro substitution product --) R Carbon number 1-4 An alkyl group or a phenyl group, and X F The compound expressed with the halogen of an except, and (B-2) general formula $R_5R_6Si(OR)_2$ or $R_5R_6SiX_2$ (here -- R5 and R6 -- a methyl group and/or a phenyl group --) R Carbon number 1-4 An alkyl group or a phenyl group, and X are F. The compound expressed with the halogen of an except is melted to an organic solvent. hydrolyzing -- having obtained -- a solution -- containing -- a silica -- a system -- porous membrane -- formation -- ** -- coating liquid -- (11) -- (A1) -- a general formula -- R -- one -- Si -- (OR) -- three -- or -- R -- one -- SiX -- three (here -- R1 -- a carbon number 2 -- the above (generally carbon number 2-12) alkyl group or its fluoro substitution product --) R Carbon number 1-4 An alkyl group or a phenyl group, and X F The compound expressed with the halogen of an except, and (A2) general formula $R_4Si(OR)_3$ or R_4SiX_3 (here -- R4 -- a methyl group or a phenyl group --) R Carbon number 1-4 An alkyl group or a phenyl group, and X F The compound expressed with the halogen of an except is melted to an organic solvent. the coating liquid for silica system porous membrane formation which hydrolyzes and contains the obtained solution, and (12) -- said coating liquid -- general formula $M(OR)_n$ or MX_n (1 as which M is chosen from B, aluminum, germanium, Ti, Y, Zr, Nb, Ta, and Si here -- the metallic element beyond a class --) n Metal M The number of the oxygen to combine, and R Carbon number 1-4 An alkyl group or a phenyl group, X F M [as opposed to Si including the compound expressed with the halogen of an except] A mole ratio is 0.005. It is 0.15 or less above. And the mole ratio of the methyl group to Si and/or a phenyl group is 0.6. It is 1.5 above. (9) characterized by being the following, (10) -- the coating liquid for silica system porous membrane formation given in (11) and (13) -- the weight average molecular weight of the solute in said coating liquid -- less than 5000 (less than 3000 preferably) [or] It is especially 500 less than further 1000. (9) characterized by being the following, (10), (11), or the coating liquid for silica system porous membrane formation given in (12), It is made to dry at the temperature below [after applying the liquid of a publication to any 1 term of (14) and (9) to (13)] 70-degree-Cor more 300 **. Next, it heat-treats in an inert gas ambient atmosphere at the temperature below 650 ** more than 350 **, and is a carbon number 2. Therefore, the manufacture approach of the silica system porous membrane characterized by carrying out the pyrolysis of the above alkyl group or its fluoro substitution product is solved.

[0009]

[Embodiment of the Invention] Generally, silica glass is connected with the next tetrahedron through oxygen at all the top-most vertices whose tetrahedrons of SiO_4 are four, and is Si-O-Si. It has the three-dimensional network which consists of a siloxane frame (drawing 1). On the other hand, since the three-dimensional network containing a siloxane frame contains what the organic radical combined with at least one of four top-most vertices of SiO_4 tetrahedron, the silica system porous membrane by this invention is glass which uses as a principal component SiO_2 containing the organic radical combined with Si, and has a detailed opening with a pitch diameter of 10nm or less in the glass. A three-dimensional network may also contain the next tetrahedron and the connected tetrahedron through bridging oxygen at all four top-most vertices of the thing which hydrogen and/or a hydroxyl group combined with at least one of four top-most vertices of SiO_4 tetrahedron other than the tetrahedron which the organic radical combined with at least one of four top-most vertices of SiO_4 tetrahedron, and/or SiO_4 tetrahedron. The opening by this invention is 77K. The adsorption isotherm of N_2 gas which can be set to the Dollimore & Heal method (DH law) When it estimates from the pore distribution curve searched for, it is 10nm or less in pitch diameter. Therefore, an opening is unobservable even if it carries out to one 500,000 times the scale factor of this with a transmission electron microscope. One example of the porous membrane of this invention is shown in drawing 2 . The porous membrane of this invention has the opening of the magnitude of the molecular level formed into the network structure as shown in drawing 2 .

[0010] Although the opening in the silica system porous membrane of this invention is an average of 10nm or less, all openings are 10nm or less substantially suitably. An opening is decided according to the pore volume distribution acquired by experiment, and pore size is equivalent to the magnitude of an opening. Moreover, the average of the magnitude of an opening is 5nm, 2nm, and 1nm by the molecular

size from which it is desorbed by the pyrolysis. Or it is also possible to make it less than [it].

[0011] Next, the specific inductive capacity of the porous membrane of this invention is described. What [what the hydroxyl group combined with at least one of four top-most vertices of SiO_4 tetrahedron] (-SiOH) When it is, they are the top where the polarizability of itself is large, and Si-OH... In order to draw the moisture in atmospheric air near by hydrogen bond like H-OH, if a silanol group exists so much, the specific inductive capacity of an ingredient will become high., i.e., a silanol group In order to prevent the hygroscopicity by the silanol group, it is thought effective to make an inorganic frame into hydrophobicity. In this invention, since it has structure which the organic radical combined with a part or all of Si in a siloxane frame, hydrophobing is carried out by the organic radical and moisture absorption can be controlled. Low dielectric constant-ization can be attained by hygroscopic reduction by the effectiveness of the reduction in a consistency by the porous membrane of such structure enclosing an opening, and an organic radical joining together and hydrophobing being carried out to a siloxane frame. The mole ratio [as opposed to / in order to give the effectiveness of the reduction in a consistency and hydrophobing / Si] of an organic radical is 0.6. It is 1.5 above. It is desirable that it is the following. This ratio is 0.6. When small, the effectiveness of the reduction in a consistency and hydrophobing is small, and it is 1.5. If large, film reinforcement will fall. When the pitch diameter of an opening exceeds 10nm, film reinforcement becomes weak and the dependability as an insulator layer is missing. For example, the problem that film peeling occurs or an abrasive grain enters into a hole when chemical machinery polish (CMP) is performed, the problem that insulation falls since diffusion of Cu used for wiring becomes quick, and the problem that there are few effective faying surface products and adhesion is bad arise. Since silica system porous membrane 10nm or less is obtained for the magnitude of an opening according to this invention, the above-mentioned problem is lost, and it is specific inductive capacity (inside of air) 2.5 It can be made the following.

[0012] The thickness of the porous membrane of this invention is 0.1. μm It is 5 above. μm It is desirable that it is the following. In order to remove conventionally the OH radical on the front face of the film which each thing known as a porous interlayer insulation film is an inorganic frame which makes Si-O a subject, and contains opening pore, it heat-treated in the controlled atmosphere, and the OH radical was permuted by the organic radical etc. (for example, US patents No.5, 470 and 802, and No.5,504,042). This invention differs from the conventional silica system porous membrane in the point that the organic radical is introduced not only into the film front face containing opening pore but into the network structure itself, by including the tetrahedron which permuted at least one or more of the bridging oxygen of SiO_4 tetrahedron which forms the network structure by the organic radical inside a front face and a frame. the conventional silica system porous membrane -- a hole -- in this invention, although the part of an except is SiO_2 , since an organic radical is included also in the network structure, parts other than a hole become organic glass, and specific inductive capacity becomes low rather than SiO_2 . For this reason, this invention can attain the same specific inductive capacity as the conventional porous membrane with voidage lower than the conventional porous membrane. Therefore, the reinforcement and dependability as porous membrane are raised.

[0013] The above-mentioned three-dimensional network is Si and O. 1 chosen as others from B, aluminum, germanium, Ti, Y, Zr, Nb, and Ta By including the metallic element beyond a class, it is expectable to lower specific inductive capacity further. 1 chosen from B, aluminum, germanium, Ti, Y, Zr, Nb, and Ta Metallic element M beyond a class Raw material [for introducing into porous membrane] M (OR) n Or MX_n Reactivity is high. For this reason, since it can react easily with the refractory silanol (SiOH) radical which exists in the film and OH of a silanol group can be removed, it is thought that specific inductive capacity can be lowered. M to Si A mole ratio is 0.005. It is desirable that it is 0.15 or less above. This ratio is 0.005. If larger [when small, the effectiveness of silanol group reduction is small and] than 0.15, specific inductive capacity will become high.

[0014] As for the organic radical which permutes at least one or more of the bridging oxygen of SiO_4 tetrahedron, it is effective that they are especially a methyl group or a phenyl group. The organic radical combined with Si is LSI. It is desired for the thermal stability of extent which can be equal also to processing of 450 ** demanded in a process and the polarizability of itself to be small. When included

in the siloxane network structure, both of methyl groups and phenyl groups have the thermal resistance to 650 **, and since polarizability is also small, they are effective as an organic radical combined with Si.

[0015] Kr gas is used for the silica system porous membrane by this invention, and it is BET. The specific surface area measured by law is 100m²/g. It is 200 morem²/g above. It is desirable that it is above. BET Although nitrogen gas is used in measurement by law in many cases, as for porous membrane, it is higher for the accuracy of measurement to use Kr with maximum vapor tension smaller than nitrogen, since the amount of adsorption is quite small. The specific surface area measured with the BET adsorption method using Kr gas is 100m²/g. When it is the following, there are few openings and the effectiveness of the specific-inductive-capacity reduction by the reduction in a consistency is small. Moreover, as for the contact angle of water, it is desirable that it is 90 degrees or more. Since in the case of less than 90 degrees hydrophobic extent is inadequate, the film shows hygroscopicity and an OH radical with high polarizability increases, specific inductive capacity increases.

[0016] Furthermore, the porosity of the silica system porous membrane of this invention is the surface area (except for the area of the side face of a substrate, and a base) S BET of the porous membrane formed on the flat-surface substrate. Area S geo which attached the film of a flat-surface substrate It means that a ratio (\Rightarrow), i.e., S BET/Sgeo, exceeds 80. this invention -- this ratio -- S BET/Sgeo 100 the above -- more -- desirable -- 120 the above -- further 150 the above -- especially -- 175 although it is above -- theoretical -- 200-300 Carrying out is also possible. In addition, it is simple to use Si wafer as a flat-surface substrate.

[0017] Moreover, the porosity of silica system porous membrane can be estimated from measurement of a film consistency before and after the organic radical of pyrolysis nature falls out. As porosity of the silica system porous membrane of this invention, it is 10% preferably. It is 15% more preferably above. It is 20 more% above. It is especially 25% or more above. If porosity is small, the effectiveness of reducing specific inductive capacity will not be acquired. Especially the upper limit of porosity is 50% at this invention, while it is thought 80% or more of generally that it is desirable, although it is not restrained but can choose suitably by relation with film reinforcement. The following also has the description from which specific inductive capacity low enough is obtained.

[0018] LSI Since the parasitic capacitance during wiring and between layers can be reduced by using the silica system porous membrane of a low dielectric constant of this invention for semiconductor devices, such as a component, as an interlayer insulation film, there is an advantage that a working speed becomes quick. The opening which the three-dimensional network which forms the porous membrane of this invention has can be formed by the pyrolysis of the organic radical combined with Si. namely, the hydrophobic organic radical (for example, methyl group) which finally remains in the film and ** -- when the organic high radical with low pyrolysis temperature (Following R pyr and publication) has combined with Si, the three-dimensional network incorporating these organic radicals is formed first. next, the hydrophobic organic radical which remains in the film and ** -- organic high radical R pyr with low pyrolysis temperature pyrolysis temperature -- respectively -- T1 and T2 (namely, T1> T2) ** - - if it carries out, it will heat-treat at the temperature between T1 and T2. By this heat treatment, it is Rpyr. Since it goes away out of the film, the marks from which it escaped remain as an opening. Thus, if an opening is formed, since a sufficiently detailed opening 10nm or less will be made in homogeneity into the film compared with wiring spacing, such as a semiconductor device, film reinforcement serves as high porous membrane. Moreover, by the organic radical which did not receive a pyrolysis but remains in the film, since membranous hydrophobicity is maintained, low dielectric constant-ization is expected. It is not necessary to necessarily decompose R pyr 100% at this time. It is 1 in the film. Rate extent and R pyr You may remain. Moreover, R pyr The part of the constituted atoms may remain and it is Rpyr. To the part into which association with Si went out, it is R pyr by decomposing. As long as it compares, since ** is small, association with the organic component which can leave an opening is performed. For example, R pyr Carbon number 2 When it is the above alkyl group, it may decompose from the carbon of an end and radicals, such as Si-CH₃ association or Si-H association, may generate into the part of the root combined with Si. Moreover, Si-Rpyr It sets to association and is R pyr. The Si

combines with other Si through oxygen after a pyrolysis, and it is Si-O-Si. Association may be generated.

[0019] Generally the pyrolysis temperature of an organic radical is the phenyl group > methyl group > carbon number 2. Organic radical R pyr to which the pyrolysis of the above is carried out since it is the above alkyl group Carbon number 2 It is desirable that it is the above alkyl group or its fluoro substitution product. Moreover, as for the organic radical which it leaves into the film, it is desirable that they are a methyl group or a phenyl group. In the silsesquioxane which constructed the bridge by the organic radical, especially the allyl group, a part of organic radical [at least] is oxidized with oxidizers, such as oxygen plasma, and the production approach of the porosity silica object which uses the marks of an organic radical as a hole is proposed (US Patents No.5,321,102). The porous body obtained by this approach is used as molecular sieves and catalyst support, and the organic radical which remained even if the organic radical remained is not used positively. On the other hand, this invention puts in two or more kinds of organic radicals beforehand, and since only an organic radical with low pyrolysis temperature is made to decompose alternatively, it can surely leave an organic radical with high pyrolysis temperature into the porous membrane finally obtained. Further, Hydrophobing of the film is carried out by the organic radical which it left into the film, The points that-izing can be carried out [a low dielectric constant] differ.

[0020] Moreover, the organic polymer of low molecular weight is distributed in methyl silsesquioxane, and the method of obtaining porous membrane is proposed by carrying out the pyrolysis only of the organic polymer by heat treatment (Julius F.Remenar, et.al., MRS 1998 Spring Meeting, Abstract p97, E2.4, US Patents No.5,700,844). It seems that it depends on the phase separation condition of SHIROKISAMPORIMA and the organic polymer of pyrolysis nature for the magnitude of the hole obtained by this approach. When an organic polymer is polymethylmethacrylate, it becomes the hole of micron order, and in the case of the poly caprolactone, it is 10nm. In this invention, since not the blend of a polymer but the pyrolysis of the organic radical coupled directly with Si is used, the porous body which has a detailed hole compared with these is producible.

[0021] The coating liquid for forming the silica system porous membrane by this invention is described. A three-dimensional network including siloxane association contains the tetrahedron which permuted at least one or more of the bridging oxygen of SiO₄ tetrahedron by the organic radical. and in order to have a detailed opening with a pitch diameter of 10nm or less directly surrounded in the perimeter by the frame containing the tetrahedron the coating liquid -- (A) or R' SiX₃ (R' -- an organic radical --) General formula R' Si (OR)₃ R Carbon number 1-4 An alkyl group or a phenyl group, and X F The compound expressed with the halogen of an except, and (B) or R -- " -- R''' SiX₂ (R -- " and R -- "' -- an organic radical --) a general formula R -- " -- R''' Si (OR) -- two R is a carbon number 1-4. An alkyl group or a phenyl group, and X F It is required to surely include either at least among the hydrolyzates of a compound expressed with the halogen of an except.

[0022] (A) The compound belonging to a group is the alkoxide which one organic radical has combined with Si, and is (B). For the compound belonging to a group, an organic radical is 2 to Si. It is the alkoxide which carried out individual association. (A) And (B) The organic radical combined with Si alkoxide of the compound of a group is 2. It is classified into a class. One is an organic radical with the effectiveness of remaining into the silica system porous membrane finally obtained, and reducing hygroscopicity. already -- 1 ** is an organic radical for introducing an opening into the film by carrying out a pyrolysis. (A), As an organic radical combined with each Si alkoxide of (B), it is this 2. It becomes the important point on the design of coating liquid how the organic radical of a class is distributed.

[0023] JP,8-3074,B is at least 2 chosen from the alkoxy run compound expressed with Q'm Si[-4-] (OQ) m (it is here and the alkyl group of a carbon number 1-3 and m are [Q'] the integer of 2-4 for the alkyl group of carbon numbers 1-3 or a phenyl group, and Q) as coating liquid for silica system coat formation. The coating liquid which melts a seed to an organic solvent, and hydrolyzes and changes is proposed. Moreover, JP,3-20377,A is 2 which the low-grade alkyl group or aryl group of carbon numbers 1-4 combined with Si. The coating liquid compounded from Si alkoxide of functionality and three functionality and the alkoxide of the various metals which the chelating agent configured is

proposed. Moreover, it sets to JP,6-346025,A and is 2. Functionality silane 1 It is 3 to a mol. The constituent for coatings of using the mixture containing 1-20 mols of functionality silanes is proposed, and hydrogen, an alkyl group, an aryl group, alkenyl radicals, and those substitution products are enumerated as a radical which is not the hydrolysis nature combined with these 2 and 3 functionality silanes. However, each of JP,8-3074,B, JP,3-20377,A, and JP,6-346025,A aims at the thick-film formation without a crack or a pinhole. In such thick-film formation, there is no concept of carrying out the pyrolysis of a part of organic component partially, conventionally, and the precise film was formed. since this invention is coating liquid for forming porous membrane using the difference of the pyrolysis temperature of an organic radical and can carry out [porous membrane]-izing -- organic [conventional / SOG] etc. -- the low specific inductive capacity which was not attained came to be obtained with a silica system coat. This invention differs from JP,8-3074,B, JP,3-20377,A, and JP,6-346025,A greatly in this point. According to this invention, it is 2.5 as specific inductive capacity in air. The following and further 2.4 The following and 2.3 The following and 2.2 The following is also possible.

[0024] first, claim 9 ***** -- it explains. (A1) general formula $R_1Si(OR)_3$ or R_1SiX_3 (for a methyl group or a phenyl group, and R, the alkyl group of a carbon number 1-4 or a phenyl group, and X are [R1] F here halogen of an except) -- (A) It is a compound belonging to a group, and it is the raw material which forms a siloxane frame at the same time it introduces the organic radical for remaining into the silica film and reducing hygroscopicity. Specifically, methyl triethoxysilane, methyl trimethoxysilane, phenyltriethoxysilane, etc. are mentioned. (B1) general formula $R_2R_3Si(OR)_2$ or $R_2R_3SiX_2$ (the methyl group or the phenyl group, and R except [R2, R at least one of 3 sorts is a carbon number 2 here. Being the above alkyl group or its fluoro substitution product.] it the alkyl group of a carbon number 1-4 or a phenyl group, and X F halogen of an except) -- (B) It is a compound belonging to a group. The compound of (B1) is a raw material for forming the siloxane frame in which the organic radical which forms an opening had combined with Si, and included the opening by pyrolyzing. Specifically as a compound of (B1), they are n-octadecyl methyldiethoxysilane, n-octyl methyldiethoxysilane, isobutyl methyl dichlorosilane, and dimethoxymethyl. - It is 3, 3, and 3. - A trifluoro propyl silane, diisobutyl dimethoxysilane, phenylethyl dichlorosilane, t-butylphenyl dichlorosilane, etc. are mentioned. Each (B1) to (A1) and 1 The compound beyond a class is chosen and the coating liquid for silica system porous membrane formation is obtained by melting and hydrolyzing to an organic solvent. For this liquid, the organic radical which is not pyrolyzed [dimethylsilane / diethoxy] other than the compound chosen out of reaching (B1) (A1) is 2 to Si. The compound which carried out individual association, and/or its hydrolyzate may also be included. Moreover, as indicated to claim 12, they are (C) or MX_n (M here). General formula $M(OR)_n$ 1 chosen from B, aluminum, germanium, Ti, Y, Zr, Nb, Ta, and Si The metallic element beyond a class, n Metal M The number of the oxygen to combine, and R The alkyl group of a carbon number 1-4 or a phenyl group, and X F Halogen of an except The compound expressed may also be included. (C) the case where come out and the compound expressed is included -- M the effectiveness which maintains film reinforcement when it is Si -- it is -- M the time of the metallic element chosen from B, aluminum, germanium, Ti, Y, Zr, Nb, and Ta -- the improvement in film on the strength -- in addition, it is effective in reducing the silanol group in the film.

[0025] Next, claim 10 is explained. (A2) general formula $R_4Si(OR)_3$ or R_4SiX_3 (R_4 is a carbon number 2 here the above alkyl group or its fluoro substitution product, and R the alkyl group of a carbon number 1-4 or a phenyl group, and X F halogen of an except) -- (A) It is a compound belonging to a group. The compound of (A1) is a raw material for forming the siloxane frame in which the organic radical which forms an opening had combined with Si, and included the opening by pyrolyzing. Specifically, they are isobutyl triethoxysilane and t-butyl trichlorosilane (3, 3, and 3-trifluoro propyl), Trimethoxysilane, triethoxysilane (trideca fluoro - 1, 1, 2, 2 - tetrahydro octyl), etc. are mentioned. (B-2) -- or $R_5R_6SiX_2$ (here -- R_5 and R_6 -- a methyl group or a phenyl group --) General formula $R_5R_6Si(OR)_2$ R Carbon number 1-4 An alkyl group or a phenyl group, and X F The halogen of an except is (B). It is a compound belonging to a group, and it is the raw material which forms a siloxane frame at

the same time it introduces the organic radical for remaining into the silica film and reducing hygroscopicity. Specifically, diethoxy dimethylsilane, dimethoxy dimethylsilane, phenylmethyldimethoxysilane, diphenyl dichlorosilane, etc. are mentioned. (A2), (B-2) Each to 1 The compound beyond a class is chosen and the coating liquid for silica system porous membrane formation is obtained by melting and hydrolyzing to an organic solvent. This liquid is (A2), (B-2) and (C). Otherwise, it is claim 9. The compound and/or its hydrolyzate which were stated by explanation (B1) may also be included. Moreover, claim 9 (C) stated by explanation A compound may also be included. (C) Effectiveness in case ***** is included is claim 9. It is as explanation having described. [0026] Next, claim 11 is explained. (A1) and (A2) are claim 9, respectively. And it is as by the way explanation of ten having stated. Each (A2) to (A1) and 1 The compound beyond a class is chosen and the coating liquid for silica system porous membrane formation is obtained by melting and hydrolyzing to an organic solvent. This liquid is (A1) (A2) and (C). By the way, claim 9 and explanation of ten explained to others, respectively (B1), The compound of (B-2) and/or its hydrolyzate may also be included. Moreover, claim 9 (C) stated by explanation A compound may also be included. (C) Effectiveness in case ***** is included is claim 9. It is as explanation having described. [0027] M [on claim 9-11 and as opposed to Si] A mole ratio is 0.005. It is desirable that it is 0.15 or less above. 0.005 If larger [when more small, the effectiveness of silanol group reduction is small, and] than 0.15, specific inductive capacity will become high. The mole ratio of the methyl group to Si and/or a phenyl group is 0.6. It is 1.5 above. It is desirable that it is the following. 0.6 When more small, the effectiveness of the reduction in a consistency and hydrophobing is 1.5 small. If large, film reinforcement will fall.

[0028] claim 13 -- setting -- the weight average molecular weight of the solute in coating liquid -- less than 5000 -- desirable -- less than 3000 and less than further 1000 -- especially -- 500 It is desirable that it is the following. Weight average molecular weight is a gel permeation chromatography (GPC) in simple. It can ask from the molecular weight distribution of the measured styrene conversion. the one where this molecular weight is small namely, where polymerization degree is lower -- ** -- organic high radical R pyr with low pyrolysis temperature The united alkoxide of Si and the hydrolyzate of a halogenide tend to make the film distributed to homogeneity. Rpyr If it is distributing to homogeneity, the opening behind produced by the pyrolysis is also distributed to homogeneity, and the magnitude is 10nm and 5nm. Two morenm and 1nm It becomes the thing of the following very small molecular levels. When with a weight average molecular weight of 5000 or more coating liquid is formed and heat-treated, it is not desirable in order that the magnitude of a hole may tend to exceed 10nm. Since polymerization degree is low, the viscosity of this coating liquid shows the Newton nature independent of a shear rate. although viscosity changes, the solute, i.e., the solid content concentration, in coating liquid, -- in general -- 0.5 - 3.0mPa and s it is .

[0029] When using an alkoxide for production of the low dielectric constant ingredient of this invention, it is beta in a part of alkoxy group. - Diketone, beta - The alkoxide derivative permuted by keto ester, alkanolamine, alkyl alkanolamine, an organic acid, etc. can also be used. By the hydrolysis in this invention, it is 2 to all alkoxy groups. The water to mol twice is added and it hydrolyzes. Under the present circumstances, an inorganic acid, organic acids, or those both may be used as a catalyst. Moreover, alkali adjusts pH of a solution, A hydrolysis reaction may be controlled. Water to add, You may dilute with organic solvents, such as alcohol. If the water beyond 2 mol twice is used, it is not desirable, in order that the life of the coating liquid used at the time of membrane formation may become remarkably short and may gel during preservation as coating liquid. [0030] It sets to hydrolysis and the organic solvent which can distribute Si raw material and metal alkoxides, such as alkyl alkoxysilane, to homogeneity, and can dissolve is used. For example, they are various alcohol, such as a methanol, ethanol, propanol, and a butanol, an acetone, toluene, a xylene, etc. After hydrolysis, It used as a solvent, Or the alcohol generated by hydrolysis may be distilled off and applied under ordinary pressure or reduced pressure. Spreading to a substrate is performed with a spray coating method, a dip coating method, a spin coat method, etc.

[0031] The spreading film is first dried by 70 - 300 **, A solvent is evaporated. heat-treating in an inert

gas ambient atmosphere at 400-650 degrees C after that -- ** -- the pyrolysis of the organic high radical with low pyrolysis temperature is carried out. As inert gas, N₂, Ar, heliums, or those mixed gas can be used. The oxygen density which prevents the contamination of the atmospheric air into a heat treating furnace during heat treatment, and is contained in inert gas in case a sample is taken in and out of a heat treating furnace is 50 ppm more preferably 100 ppm or less. The following and 20 more ppm It is desirable to make it below. It is that heat treatment temperature is under 350 **, Since decomposition of an organic radical with low pyrolysis temperature does not take place, an opening is not made and specific inductive capacity does not fall enough. 650 If ** is exceeded, since all organic radicals will decompose, hygroscopicity will become remarkably high and specific inductive capacity will increase by the OH radical in the film.

[0032] The insulator layer by this invention, and LSI It is applicable to semiconductor devices and various electronic parts, such as an interlayer insulation film for components. Moreover, it is available also as catalyst support.

[0033]

[Example] The following examples explain the low dielectric constant ingredient of this invention concretely. (Example 1) They are dimethoxymethyl 3 and 3 and 3-trifluoropropyl trimetoxysilane in ethanol 2 It is [what was beforehand hydrolyzed with twice / mol / as many water as this, an ethyl acetoacetate and the alt.titanic-acid tetraethyl made to react, and] methyl triethoxysilane at a mole ratio 12:1:24 It mixed in the ethanol solvent so that it might become. It hydrolyzed with twice as many 70-mol water as this to alt.titanic-acid tetraethyl after mixing. the viscosity of this coating liquid -- E the place measured with the mold viscometer -- the rotational speed of a cone rotor -- 10rpm from -- the range of 100rpm -- 1.95mPa(s) and s it was . Next, this coating liquid is dissolved in a tetrahydrofuran and it is GPC. The molecular weight of styrene conversion was calculated. The molecular weight distribution seen from UV absorption are shown in drawing 3 . Two big peaks are molecular weight 120. It existed in the place of the neighborhood, and was not solvents, such as ethanol and a methanol, but was a thing originating in the alkoxide of Si. The hydrolyzate of the alkoxide of the solute in coating liquid, i.e., silicon, and titanium is understood that polymerization degree is very low. thus, Si wafer top with which platinum attached the adjusted liquid as a lower electrode to electric capacity measurement - FT-IR the hot plate top set as each temperature of 70 degrees C, 150 **, and 200 ** after membrane formation by the spin coater on Si wafer for measurement, respectively -- one every -- this order was dried. Next, it heat-treated by 450 during 20 minutes ** among nitrogen-gas-atmosphere mind with the electric furnace.

[0034] FT-IR Although it had become the structure with which a methyl group and -CH₂CH₂CF₃ went into SiO₂ film from the spectrum before heat treatment of 450 **, after heat treatment, it turned out that -CH₂CH₂CF₃ pyrolyzes till disappearing [the peak originating in CF association]-completely time, and only the methyl group has structure which entered into the film. Kr gas -- using -- BET although it was the precise film which is in agreement with the specific surface area calculated from the geometrical configuration of a wafer before heat treatment of 450 ** when specific surface area was measured by law -- the film after heat treatment -- film weight -- converting -- specific surface area -- 260m²/g it was . the ratio of membranous surface area and the substrate area for which it asked from the magnitude of Si wafer -- S BET/S_{geo} 175 it was . the consistency of this film -- 1.2 it was . heat treatment during 380 **20 minutes in nitrogen -- carrying out -- CH₂CH₂CF₃ the time of making the film which did not pyrolyze but all remains -- a consistency -- 1.5 it was . the porosity for which it asked from change of a film consistency -- about 20% it was . These experimental results show that the film obtained by 450 ** processing includes the detailed opening produced by the pyrolysis of an organic radical. Pore volume distribution is 77K. It asked by the DH process from the adsorption isotherm of N₂ gas which can be set. Pore size is 5nm. It is distributed over the following fields and a peak is 2nm. It existed near. Moreover, a flake with a thickness of about 10nm is produced and it is TEM. 400 The hole was not seen although observed by one 10,000 times the scale factor of this. 5nm The hole of extent is TEM. Since it is observable, the hole of the film by this invention is considered to be a detailed thing not more than it. The film is stripped and they are ²⁹Si and ¹³C. NMR 3 contained in -CH₂CH₂CF₃ as a result of

measuring C of a class The belonging peak disappears by heat treatment of 450 **, and is C of -CH₃. It was accepted and it turned out that it remains. About Si nucleus, a methyl group is after heat treatment of 450 **, and all Si is 1. It had become poked T3 type (association with Si through O is a 3 ***** Si nucleus).

[0035] the thickness of the produced film -- about 500nm it was . After heat treatment, A sample is left for one week in the usual desiccator, and it is the diameter of 1mm. aluminum electrode is attached as an up electrode, Electric capacity was measured in atmospheric air and a vacuum with the impedance analyzer. the place which computed specific inductive capacity from this result -- the specific inductive capacity in the inside of atmospheric air -- the specific inductive capacity in the inside of 2.3 and a vacuum -- 2.2 it was . Difference of the dielectric constant in the inside of atmospheric air and a vacuum, It means that the moisture in atmospheric air adsorbs into the film. The dielectric constant of the silica film is 4 generally. As opposed to being the following, Since the dielectric constant of water is 80 at 20 degrees C Even if it is little adsorption A dielectric constant is influenced greatly, It becomes the index of hygroscopic evaluation of a minute amount., The difference of the dielectric constant by the moisture absorption in this example is very small as porous membrane at 4%. Since the methyl group is incorporated in the film, the film itself becomes hydrophobicity and this is considered because moisture cannot enter easily. As a result of measuring with a contact angle plan, the contact angle of water is 101. It is whenever and checked that it was hydrophobicity considerably.

[0036] (Example 2) They are an ethyl acetoacetate, the alt.titanic-acid tetraethyl made to react beforehand, methyl triethoxysilane, and isobutyl triethoxysilane at a mole ratio 1:1:5 It mixed in the ethanol solvent so that it might become. It hydrolyzed under the hydrochloric-acid catalyst with twice as many ten-mol water as this to alt.titanic-acid tetraethyl after mixing. thus, the hot plate top set as each temperature of 70 degrees C, 150 **, and 200 degrees C after membrane formation by the spin coater on Si wafer for FT-IR measurement, respectively on Si wafer with which platinum attached the adjusted liquid as a lower electrode to electric capacity measurement -- one every -- this order was dried. Next, it heat-treated by 450 during 30 minutes ** among nitrogen-gas-atmosphere mind with the infrared oven.

[0037] FT-IR Although it had become the structure with which the methyl group and the isobutyl radical went into SiO₂ film from the spectrum before heat treatment of 450 **, after heat treatment, it turned out that an isobutyl radical pyrolyzes till disappearing [the peak originating in an isobutyl radical]-almost time, and only the methyl group has structure which entered into the film. It is guessed that the film which included from this the detailed opening produced by the pyrolysis of an isobutyl radical is made.

[0038] the thickness of the produced film -- about 600nm it was . After heat treatment, A sample is left for one week in the usual desiccator, and it is the diameter of 1mm. aluminum electrode is attached as an up electrode, Electric capacity was measured in atmospheric air and a vacuum with the impedance analyzer. the place which computed specific inductive capacity from this result -- the specific inductive capacity in the inside of atmospheric air -- the specific inductive capacity in the inside of 2.45 and a vacuum -- 2.3 it is -- the hygroscopic small film was obtained with the low dielectric constant.

[0039] (Example of a comparison) They are dimethoxy dimethylsilane, methyl trimetoxysilane, and a tetramethoxy silane 1:1:2 in ethanol It mixed and hydrolyzed with twice [equimolar] as many water as this to all alkoxy groups. It heat-treated in 30-minute nitrogen by 400 ** after membrane formation / desiccation like the example. FT-IR The spectrum showed that the methyl group of tales doses was mostly contained into the film with the preparation presentation. BET The measurement result of the specific surface area by law showed that it was the precise film.

[0040] specific inductive capacity -- the inside of atmospheric air -- the inside of 3.0 and a vacuum -- 2.8 it was . Although the methyl group is contained as an organic radical into the silica, since there is almost no opening, this film is a dielectric constant 2.5 It was not able to lower to the following.

[0041]

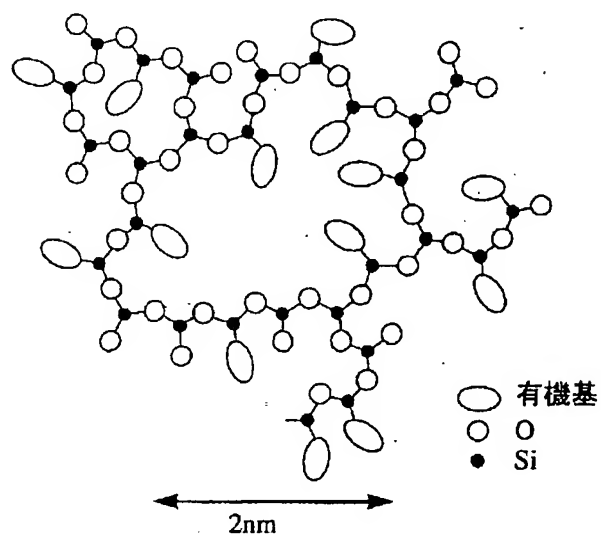
[Effect of the Invention] According to this invention Specific inductive capacity is 2.5. It is as low as the following, Silica system porous membrane also with low hygroscopicity was obtained. LSI This low dielectric constant ingredient is applied to a semiconductor device and electrical circuit components, .

such as the ** interlayer insulation film, Since delay of an electrical signal becomes small, it can respond to improvement in the speed of a device.

[Translation done.]

Drawing selection [Representative drawing]

図 2



[Translation done.]